SYRACUSE UNIV N Y DEPT OF CHEMISTRY
PHOTOCHEMICAL DISSOCIATION FROM SELECTED ROVIBRONIC STATES IN P--ETC(U)
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

This report summarizes the results of a study which was intended to provide a clearer understanding of the relationships between the pathways for photodissociation of gas phase, polyatomic molecules and the quantum states into which they are initially excited. The study characterized these relationships by examining the absolute and relative efficiencies for dissociation along specific pathways leading to particular products. The parent molecule was, in general, prepared by excitation in single vibronic levels (SVL) in which a broad, undefined distribution of rotational levels was simultaneously normalated.

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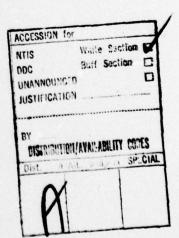
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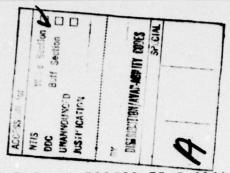
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## Research Papers Published under ARO-D Grant DAAG29-75-G-0104

- "Time-Resolved Single Vibronic Level Fluorescence Spectroscopy: Glyoxal," E. Photos and G. H. Atkinson, Chem. Phys. Letters 36 34 (1975).
- 2. Quantitative Intracavity Laser Detection of NO<sub>2</sub> by Optical Multichannel Analysis, "G. H. Atkinson, T. N. Heimlich, and M. W. Schulyer, J. Chem. Phys. 66 5005 (1977).
- 3. "Selected-state Photodissociation of Glyoxal: Vibronic Effects in the Quantum Yields of CO," G. H. Atkinson, M. E. McIlwain and C. G. Venkatesh, J. Chem. Phys. 68 726 (1978).
- 4. "Absolute Quantum Yields of CO For Selected-state Photodissociation," G. H. Atkinson, M. E. McIlwain, C. G. Venkatesh, and D. M Chapman J. Photochem. 8 307 (1978).
- 5. "Laser Bandwidth and Wavelength Stability Measurements Using Self-scanning Linear Diode Arrays," T. H. Shake, M. E. McIlwain, and G. H. Atkinson, Appl. Spectros. (in press).
- "Vibronic Analysis of TRSVL Fluorescence Spectra from Glyoxal: General Activity," G. H. Atkinson, R. A. Malstrom, and M. E. McIlwain, J. Molec. Spectros. (in press).
- 7. Vibronic Analysis of TRSVL Fluorescence Spectra from Glyoxal: Activity in  $\nu_6$ ," G. H. Atkinson, R. A. Malstrom, and M. E. McIlwain, J. Molec. Spectros. (in press).

#### Manuscripts in Preparation

- 8. "Vibronic Analysis of TRSVL Fluorescence Spectra from Glyoxal: Combination Bands and Excited-State Perturbations," R. A. Malstrom and G. H. Atkinson.
- "Quantum Yields of CO from Single Vibronic Levels in Formaldehyde,"
   M. E. McIlwain and G. H. Atkinson.
- 10. "TRSVL Spectroscopy of Propynal," L. Johnson and G. H. Atkinson.
- 11. Time-dependence for HCO Production for Acetaldehyde by Intracavity Laser Detection, R. J. Gill, W. Johnson, and G. H. Atkinson.

### Final Report

This research program was intended to provide a clearer understanding of the relationships between the pathways for photodissociation of gas phase, polyatomic molecules and the quantum states into which they are initially excited. The study characterized these relationships by examining the absolute and relative efficiencies for dissociation along specific pathways leading to particular products. The parent molecule was, in general, prepared by excitation in single vibronic levels (SVL) in which a broad, undefined distribution of rotational levels was simultaneously populated.

The study was especially concerned with primary dissociative processes. Samples were examined at low pressures where the degree of collisional perturbations was minimized and therefore, the initially-populated quantum states were largely preserved prior to dissociation. Attention was also focused on the excited-state redistribution processes which occur following state-selective excitation. The analysis for dissociation products was concerned with transient species as well as stable molecules in order to learn as much about the channels which compete in the dissociation of the parent.

At the outset of this research project, many of the techniques for performing these measurement were not available. As a result, a significant part of our work focused on the design and development of new experimental techniques. These include (1) quantitative vacuum ultraviolet resonance fluorescence measurements of submicron CO

concentrations for absolute quantum yield experiments [1-4], (2) time-resolved single vibronic level (TRSVL) fluorescence spectroscopy to obtain information on the excited-state populations and energy transfer mechanisms occurring subsequent to state-selective excitation [5-9], and (3) intracavity laser detection of free radical products [10-11]. The application of these techniques to a variety of molecular systems has led to a wide range of significant new findings.

### A. Quantum Yields of Stable Products

The quantum yield of a stable product provides indirect information about the primary dissociation pathways. By using SVL excitation and making the measurement of the product yield at low (millitorr) pressures, we have attempted to extend the enormous amount of previous work on photochemical quantum yields obtained at high pressures. Since only a few millitorr of product were required for a quantum yield measurement, the initial stages of dissociation could be examined for samples at pressures where collisional perturbations could be minimized [2]. Thus, the intially-populated SVL could be preserved long enough to influence the dissociation processes. This influence could then be observed in the dependence of the quantum yield of a stable product on the SVL initially excited.

A study in glyoxal demonstrated that precisely this type of relationship could be observed. The absolute quantum yield of CO (  $\phi_{CO}^{abs}$ ) exhibited a dramatic dependence on the SVL excited, changing by more than 40% [1]. This state-selective dissociation indeed persisted at

pressures up to 10 torr and represented the first such dependence observed for a polyatomic molecule. Distinctive pressure dependence ences were also observed. These results were interpreted in terms of an excited-state mechanism which contained an important role for vibrationally-excited triplets not previously recognized.

A comparison study in formaldehyde provided a contrasting example. No strong state-selective effects were observed in  $\phi_{CO}^{abs}$  [3]. Rather, a wavelength onset for CO production occurs. When the pressure dependence of CO for SVL excitation is measured, however, one does observe that levels involving three quanta of  $\nu_*$  show a decrease in  $\phi_{CO}^{abs}$  below 1 torr which is not seen for other SVL [3].

The differences in the relationships between  $\phi_{CO}^{abs}$  and the SVL excited for glyoxal and formaldehyde reflect the fact that two distinct pathways control dissociation. Collisionally-induced  $^{1}A_{u}^{-3}A_{u}$  intersystem crossing operates in glyoxal while  $S_{1}$ - $S_{0}$  internal conversion apparently precedes dissociation in formaldehyde. The first process can preserve state-selective excitation while the second does not. These two molecular systems represent two classification of state-selective photodissociation in polyatomics.

The mechanisms by which state-selective population in excited states are preserved can also be examined by TRSVL fluorescence spectroscopy [5]. By simultaneously resolving the emission from a SVL with respect to wavelength and the time after excitation, one can both identify the vibronic characteristics of the excited-state level fluorescing and measure the time-dependent flow of energy within

the excited state. Studies of glyoxal have established that the <sup>1</sup>A<sub>u</sub> population present prior to dissociation into CO does indeed fulfill the requirements for preserving the state-selective nature of the excited state [1]. An extensive study of the TRSVL spectroscopy of glyoxal [6-8] has also (1) confirmed the <sup>1</sup>A<sub>u</sub> vibronic level populated by excitation into over forty absorption bands (2) revealed the activity of previously unrecognized vibrational modes, and (3) pinpointed the presence of numerous excited-state perturbations. All of these data have a direct bearing on the accuracy of SVL photodissociation studies. Attempts to measure the level-to-level vibrational relaxation rates in polyatomic molecules by TRSVL fluorescence technique were also initiated and are currently underway [12].

# B. <u>Time-Resolved Measurements of Short-lived Products</u>

Time-resolved measurements following pulsed excitation of a molecule into a SVL is a more direct method for learning about primary dissociation processes. Two methods for obtaining such data were used in this program: (1) vuv resonance emission and (2) intracavity laser detection (ILD).

Time-resolved fluorescence signals from CO in the photolysis of glyoxal were obtained by the vuv method, but since instrumentation required for extensive signal averaging was not available, no time-dependent concentration measurements were possible.

ILD techniques, however, have been exceedingly successful at measuring transients. Based on the principles of gain-spoiling within an optical resonator of a laser, ILD requires the detected species only to absorb and not emit. Thus, predissociated free radicals

such as HCO which do not fluoresce strongly can be observed readily by ILD. Indeed, the first time-resolved study of HCO kinetics was obtained during this work in the photolysis of acetaldehyde and glyoxal [11].

In the photodissociation of acetaldehyde, HCO (0,0,0) reaches a maximum concentration 200  $\mu$ sec after excitation [11]. This represents the combined time for dissociation and vibrational relaxation within HCO down to the zero point level monitored in these experiments. Nonetheless, quenching studies demonstrate that about 100  $\mu$ sec in due to a time delay within the parent.

Somewhat similar delay time are observed in other aldehydes. In glyoxal, for example, HCO (0,0,0) appears at maximum concentration at about 80 µsec after excitation [11]. The state-selected mechanisms for producing HCO and the subsequent reactions of the radical are currently being pursued by ILD. Analogous studies of NH<sub>2</sub>, NO<sub>2</sub>, CH<sub>2</sub> and a variety of larger polyatomic radicals are also underway.

#### Conclusions

The research program funded under this grant has provided a wide range of new experimental techniques (TRSVL spectroscopy, ILD, and quantitative vuv resonance fluorescence) and data concerning the state-selective effects of photophysics and photochemistry in gas phase, polyatomic molecules. The techniques have expanded our experimental capabilities for observing the dynamics of fast, excited-state reactions such as photodissociation. The results on the quantum

yields of products, time-resolved vibrational energy redistribution within excited electronic states, the time of appearance for free radical products together with their internal energy distributions, and the correlation of each of these types of data with the initial quantum states of the reacting parent molecule all point to conclusion that even simple, "well-understood" polyatomic molecules undergo exceedingly complex mechanisms to affect dissociation. A common part of these complex mechanisms, in at least the systems examined here, is the appearance of products in extremely nonequilibrated state distributions. This behavior warrants careful future study for at least one practical reason: the improvement in efficiency for the photodissociation method of operating chemical lasers. There are, of course, numerous more fundamental principles of reaction dynamics in the gas phase which are explored in such work. This initial period of our work has begun to identify a few of the fruitful areas for study and has provided a few new tools for doing so.

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